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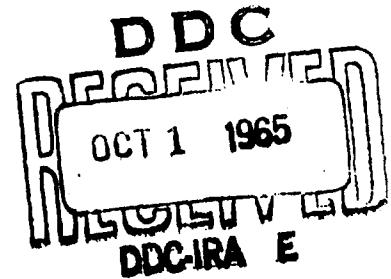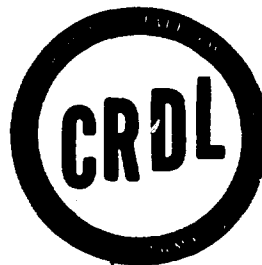| |
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REPORT NUMBER 4

RESEARCH STUDY OF NEW CONCEPTS TO PROMOTE
THE FAILURE OF POLYMERS BY STRESS CRACKING

QUARTERLY PROGRESS FROM 1 APRIL 1965 TO 30 JUNE 1965

W.E. Wolstenholme
C.F. Stark
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July 1965

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US Army Edgewood Arsenal
CHEMICAL RESEARCH AND DEVELOPMENT LABORATORIES
Edgewood Arsenal, Maryland 21010

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UNITED STATES RUBBER COMPANY
Research Center
1361 Alps Road, Wayne, New Jersey 07470

REPORT NUMBER 4

RESEARCH STUDY OF NEW CONCEPTS TO PROMOTE
THE FAILURE OF POLYMERS BY STRESS CRACKING

QUARTERLY PROGRESS FROM 1 APRIL 1965 TO 30 JUNE 1965
INCLUDING
REVIEW OF FIRST YEAR'S WORK

W.E. Wolstenholme
C.F. Stark
V.P. Tomaselli

July 1965

US Army Edgewood Arsenal
CHEMICAL RESEARCH AND DEVELOPMENT LABORATORIES
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FOREWORD

The research work reported herein is authorized by Task
1C522301A06103, Chemical Antimateriel Agents (U). Work
was started on this contract 1 July 1964.

Acknowledgments

In addition to the authors, W. E. Wolstenholme, C. F. Stark,
and V. P. Tomaselli, the following personnel also worked on
this problem: R. F. Paddock.

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DIGEST

The purpose of this research study is to develop a new concept on the failure of polymers by stress cracking. New basic information is desired to aid in the discovery of catalysts, chemical agents, or physical methods that will markedly accelerate the failure of polymers by stress cracking. The studies will be directed towards the formulation of a detailed mechanism of failure that takes into account the influence of the environment, the chemical structure, molecular properties, and external conditions, such as temperature and applied stress. Requirements of experimental conditions and formulation of mathematical analysis for investigation of the physical degradation will be an integral part of this study. The ultimate objective is to obtain leads that will disclose agents and methods for antimaterial agents and techniques.

Progress on the Research Study of New Concepts to Promote the Failure of Polymers by Stress Cracking has been made in several of the specific areas of this problem. The experimental conditions required to test the failure produced by stress cracking has been reduced to practice. The development of analytical concepts and relations of the molecular properties involved in the failure phenomena with the composition of the polymers and the influence of the environment are being related to known properties such as surface properties, intermolecular energies and the failure mechanism based on a reaction rate process. Investigation of catalytic chemicals such as cracking agents has shown that the failure life can be shortened by a factor of 10^7 for vulcanized elastomer tread stocks. In addition to molecular properties of the cracking agents, the molecular structure appears to have an influence on the effectiveness of cracking agents. Future work will be directed towards improvement of the elementary concepts and approximations now used. Studies on the influence of molecular structure of cracking agents will continue. The failure characteristics for dynamic low stress conditions will be investigated in hostile environments for simulation of antimaterial agents on automotive treads as well as other polymeric materials.

Results presented in this report cover the following work. Experiments have shown that failure time of treated samples is not influenced by sample size. Sets of material parameters for untreated and treated samples of SBR tread, Butyl tread and polyethylene have been obtained. Exploratory trials of cracking agents on Butyl tread produce a 10^7 reduction in failure time as was found for SBR tread. Cracking agents effective on tread stocks have little effect on polyethylene. An accelerated test for cracking effectiveness is being developed. Surface properties of polymers appear to have a specific influence in cracking effects. Computation of surface energy of polyethylene by three methods is in fair agreement and has established an important guideline in the mechanism of failure. Calculation methods for surface energies of binary mixtures was used to evaluate surface energy at maximum swelling of a vulcanized SBR stock. Experiments on spreading of organic liquids on SBR tread were used for an estimate of surface tension of the tread stock. Comparison of surface tension and solubility parameters of various polymers was made to show agreement with computed surface tension of SBR tread. Cracking tests with substituents on benzene ring are as effective as benzene.

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TECHNICAL DISCUSSION

Introduction

This report contains a review of the work accomplished in the pre-
vious four quarters of the first years work and a regular detailed prog-
ress report on the work of the fourth quarter.

Statement of the Problem

The objective of this research study is to obtain basic in-
formation that will provide leads toward the discovery of new catalysts,
chemical agents of physical methods which will markedly accelerate the
failure of polymers by stress cracking. This study is to include, but
not be limited to: (1) a study of the mechanisms involved in failure
by stress cracking, (2) an evaluation of experimental conditions re-
quired to test this failure, (3) the development of analytical concepts
and relations of the molecular properties involved in the failure phen-
omena with the composition of the polymers and the influence of the
environment, including effects of normally abundant chemicals, and (4) an
investigation of catalytic chemicals or physical effects that could lead
to the discovery of antimaterial agents or techniques.

Background

The well-known dependence of the useful life or time to
failure of a material on the imposed stress and temperature indicates
that the process or mechanism causing failure is a property of the
material associated with its composition and structure. Also, the time
to failure can be markedly influenced by so-called environmental changes.
Practical experience has shown that the failure times of materials can
be delayed by surface films such as paint or other films and that such
protection of the surface increases the useful life of a material in a
hostile environment. This means that properties, conditions and events
at the surface of the material and the surface interaction with cracking
agents are of importance in the mechanism that determines the useful
life of a material.

Method of Approach

The large changes produced by controlled variations of
applied stress over a range of temperatures in the failure life of
materials have been used to evaluate the material parameters of im-
portance in the failure process. With the use of suitable modifica-
tions[1] the failure process can be analyzed in terms of a general
reaction rate process. This analytical method provides the set of

material parameters that characterize the failure process independent
of stress and temperature. Interpretation of material parameters in
terms of molecular mechanisms associated with the failure process was
developed as equivalent to the intermolecular cohesion properties of
thermodynamics. Environmental surface treatments produce large changes
in the time to failure and the material parameters exhibit variations
dependent on the environment. Work is now in progress to determine
what surface properties are altered by the environmental substance and
what molecular properties of different environments are related to the
characteristic changes experimentally observed. Compilation and cor-
relation of these properties will provide the ground rules that will
guide the selection of antimaterial agents.

General

This review sketches the main features of the work on this problem for the four quarters ending June 30, 1965. The performance is not described in chronological order but as a narrative review of the developments that have been achieved in the several categories covering the work. Specific details on most items are not individually referenced, however, at selected paragraphs, reference is made to the appropriate quarterly progress reports as the source for further detail.

Test Apparatus and Techniques

Development of inexpensive experimental test apparatus and techniques covering both static and dynamic test conditions has been a necessary part of this work.

The eccentric roller type clamps were found to be suitable for holding a conventional dumbbell shaped test piece under constant load for long periods without jaw slippage or breaks. Samples are die cut from press-molded slabs and loaded in tension to a desired stress level based on the original cross-section. The time to failure or stress rupture time is recorded by an electric timer. When the sample breaks a string attached to the falling weights opens a switch in the timer circuit. Test units in thermostalled ovens with loading weights and timer outside the oven are used for tests at elevated temperatures (Report #1).

Environmental conditions are simulated by use of liquid cracking agents. A swab of cotton is wrapped around the narrow stressed section of the sample and is held in place by a small ribbon of aluminum foil which is finger-pressed around the sample. Cracking solutions are applied to the cotton tuft with an eye dropper. Volatile agents required frequent reapplication in long term testing (Report #1).

The influence of sample size was tested by varying the cross-sections from .125" x .080" to 1.00 x .080". At equivalent stress levels with benzene as the cracking agent, no specific influence of sample cross-section was observed (Report #4).

Dynamic testing using a flexural cut-growth test has shown that cracking agents greatly reduced sample life as found in static stress rupture tests.

Material Parameters from Stress Rupture Life Data

Stress rupture testing is a common means of determining the failure or stress rupture life of a material. In these tests it is well known that the lifetime of a material will decrease as the stress level is increased at constant temperature or will decrease as the temperature is increased at constant stress. This effect of stress and temperature on service life is a recognized fact in practical use of materials.

An analysis of the failure time can be developed in terms of a mechanism that starts at the time of initial loading and proceeds to completion at the time of rupture. The rate of this process is described by a reaction rate equation which with suitable modifications is used to describe the stress rupture test data. The integrated equation for the failure time is

$$\ln t_f = \ln \left[\frac{h}{2k} \quad \frac{N}{T}\right] + \frac{\Delta F}{RT} + \frac{\lambda q}{2k} \frac{S}{T} \qquad (1)$$

with three external measurable variables,

t_f = failure time, secs
T = test temperature, degrees Kelvin
S = stress on specimen, dynes/cm^2

and three parameters,

ΔF = activation energy, kilocalories/mol of active elements
N = frequency factor, pure number
λq = volume of unit moving, cm^3

and the constants

$h = 6.5 \times 10^{-27}$ erg sec. (Planck constant)
$k = 1.37 \times 10^{-16}$ erg/deg. (Botlzmann constant)
$R = 1.98$ cal./deg. (gas constant)

At constant temperature, T_1, equation (1) reduces to

$$\ln t_f = A_1 + b \, S/T_1 \qquad (2)$$

and on semi-log plots, the stress rupture time would be linear as a function of the ratio, S/T_1. If the temperature is increased to T_2 and if the three parameters remain constant, then A_2 will be less than A_1 and the slope b will remain constant, whence the line depicting failure times at T_2 has shifted inward towards the origin as shown in the diagram. At any value of constant stress, the sample life at the higher temperature is less than at the lower temperature. These lines are also termed stress isothermals.
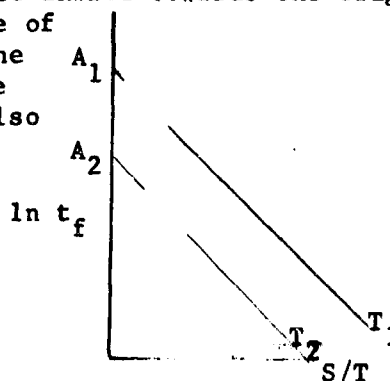
Experimental work has shown that the stress rupture life of vulcanized elastomers, namely SBR tread, Butyl tread and polyethylene can be evaluated by this technique. The material parameters for these materials have been determined for normal or untreated samples tested in air (Reports 2, 3, 4).

Application of an environmental condition by applying crack-ing agents is equivalent to a temperature increase. As an example, the stress isothermal for specimens treated with cracking agents at tempera-ture T, will be a line closer to the origin with, as experiments have shown, the same slope. The meaning of constant slope is that the mat-erial parameter, λq, is unchanged. But the constant A_1^1 for the iso-thermal of the treated stock has changed and this means that the mat-erial parameters, ΔF and N have changed due to the effect of the crack-ing agent on the stress rupture life (Reports 2, 3, 4).

Molecular Mechanisms in the Failure Process

The pictorial concept of the failure mechanism can be des-cribed in terms of the three material parameters of equation (1). The volume element, λq, is taken as the mean volume of groups of molecules that move in adjustment to the internal conditions created by condi-tions of stress and temperature. Such movement is considered similar to the well-known dislocation movement of a distorted section in crystals. The present interpretation of the calculated elemental volume, λq, is that the time-to-failure involves dislocations of molecular groups that can be represented in terms of a mean volume by the term, λq.

The movement of these volume elements means that the in-cremental volume elements must expend or overcome an energy barrier which for a mol of such units is taken as equivalent to the activation energy, ΔF, of the failure process. The total number of events to failure is the number N which is called the frequency factor. Both ΔF and N are changed by use of cracking agents in stress rupture. However, our experimental data are still not sufficient to properly state whether the action of cracking influences both ΔF and N equally or one of the parameters more than the other.

Failure or breaking of a specimen means that intermolecular properties are of importance. Since the activation energy is considered as a measure of the intermolecular properties, i.e. the intermolecular cohesion, a comparison between ΔF and intrinsic molecular properties such as the cohesive energy density was made. A basis for a comparison between activation energy and the cohesive energy density can be formu-lated by the following considerations. The failure process proceeds to completion by the movement of molecular volume elements that adjust, overcome or do work against the attractive forces existing between the surfaces of these elements. Since the activation energy is a measure of this energy barrier, then the attraction energy per volume element can be computed. But this energy is effective over the surface, hence, the energy per unit of surface on the volume element is obtained by dividing by the two-thirds power of the elemental volume. A similar computation is made using the cohesive energy density obtained from the solubility parameter and the estimated molar volume.

The assertion that the attractive forces expressed as the cohesive intermolecular energy is the same as the intermolecular energy barrier as measured by the activation means that these two energies on a proper unit basis should be unity or

$$\frac{\text{energy per unit of molecule surface}}{\text{energy per unit of } (\lambda\, q) \text{ surface}} = 1$$

Although the hypothesis used in developing this relation contains many simplifying assumptions and some additional simplifications are used in evaluation of this ratio, the value for SBR tread stock was 2.77. This was considered remarkably good agreement in view of the crude estimates used in the evaluation (Report 3).

The major point of importance is that one of the material parameters computed from the reaction rate analysis of the failure process can be associated with a known molecular property. This has opened a large field for further analytical progress to develop the technology of the failure of materials on a firm basis.

Molecular Structure in the Failure Process

Experimental work on samples treated with cracking agents has demonstrated that the stress rupture failure times of tread stocks can be decreased by a factor of 10^7 at room temperature. This effect was gained by noting the general correlation between properties such as the solubility parameters of the polymer used in the tread stock and of the cracking agent. Further improvement or enhancement of cracking effectiveness was achieved by noting that certain types of molecular structural arrangement in chemicals used as cracking agents were, under equivalent conditions, more effective than others which had similar solubility characteristics. At present the available information on the influence of molecular composition and architecture of cracking agents in reduction of failure times is not large. The aromatic ring structure of hydrocarbons is more effective in cracking of SBR tread than the paraffinic linear chain hydrocarbon although some substituted halogen linear compounds, namely, trichloroethylene and chloroform, show failure results that approach the performance of the aromatics. Present indications are that both molecular structure and the molecular force field as expressed by properties called the solubility parameter are of importance in the failure process.

Surface Properties in the Failure Process

The surface properties of a material arise from the molecular composition and structure which, of course, are the source of the internal forces and strength properties of the material. The expectation that surface and bulk properties are related is confirmed in modern science which has shown for a simple ideal case that the surface energy can be equated to the vaporization energy or the cohesive energy between molecules. These concepts were used to calculate the surface energy of an SBR tread stock with surprisingly good results when compared with similar results from surface tension measurements.

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The follow-through to surface energy properties is considered
a natural consequence in view of the fact that cracking agents applied to
a stressed surface reduce the service life of the stressed material. The
surface properties involved are the surface tension which in effect is
the energy to wet or spread on the surface, the relative number of sur-
face discontinuities suitable for stress concentration to start a crack,
stress, temperature and possibly other variables as yet unstated. Work
is now being continued on the influence of binary mixtures for this is
the surface condition when a cracking agent is applied to the surface
of a stressed polymer (Report 4).

Exploration of the technical aspects of the contribution of
surface properties in changing the failure times has just started. In
the initial stages progress will be slow because there is a dearth of
experimental data in this field. As a consequence, each new idea must
be supported by experimental trials for evaluation of the behavior exhi-
bited when polymer surfaces are exposed to cracking agents.

Achievements in Fiscal 1965

Progress on the Research Study of New Concepts to Promote
the Failure of Polymers by Stress Cracking has been made in several of
the specific areas of this problem. The experimental conditions re-
quired to test the failure produced by stress cracking has been reduced
to practice. The development of analytical concepts and relations of
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structure of cracking agents will continue. The failure characteris-
tics for dynamic low stress conditions will be investigated in hostile
environments for simulation of antimaterial agents on automotive
treads as well as other polymeric materials.

Part I

Testing Techniques

Influence of Sample Size on Environmental Stress Cracking

The effect of sample size on test results must always be examined to insure the reliability of any generalizations or conclusions drawn from the data. In recent stress rupture tests[2] of SBR tread samples treated with cracking agents, the failure times at stress levels less than 10% of the tensile breaking stress showed appreciable scatter. Although there was no doubt about the effectiveness of environmental treatments in reducing the time to failure, the suggestion was advanced that in the low stress region there may be a lesser number of micro-cracks opened on the surface of the samples. This could materially alter the attack of the cracking agent since the concept that cracking agents promote the failure process at discontinuities on the stressed surface has been an integral factor in the development of failure mechanisms.

In all previous experimental work for determining the material parameters and the effectiveness of cracking agents in decreasing failure time, the dumbbell type samples used in the stress rupture tests were die-cut specimens from sheet stock .080" thick with a 1/8" die. Some preliminary observations suggested that surface cracks, presumably produced by die-cutting, appeared to be one of the main causes for scatter of low stress level failure times. On this 1/8" sample the portion of the sample surface cut by the die is 40% of the total surface exposed to the cracking agent.

A set of experimental conditions were devised to test the influence of sample size on failure time. The ratio, P/A, of the perimeter to the cross-section area of the 1/8" die-cut sample is 41. From sheets of the same thickness, samples were die-cut with a 1/4" die, a 1/2" die and a 1" die. The P/A ratios for these samples are 33, 29, 27 respectively. Also, the percentage of die-cut surface to total surface exposed decreases to 24%, 7.2% and 1.35%, respectively. Any influence of die-cut surface or of sample surface to cross-section area on failure time would tend to give longer times to failure as the sample size increases.

Stress rupture tests were run on these samples with benzene as the cracking agent. Loading was adjusted to obtain low stress levels in the range from 180 psi to about 500 psi. All tests were at room temperature. The results are shown in Figure 1 as a semi-log plot of lot t (time to failure, secs.) as a function of the ratio of stress level over temperature. The line depicting the behavior of the 1/8" die-cut samples is from previous work[2] The dashed lines shown on the figure are drawn at the same slope as the solid line.

INFLUENCE OF SAMPLE SIZE ON STRESS RUPTURE FAILURE OF

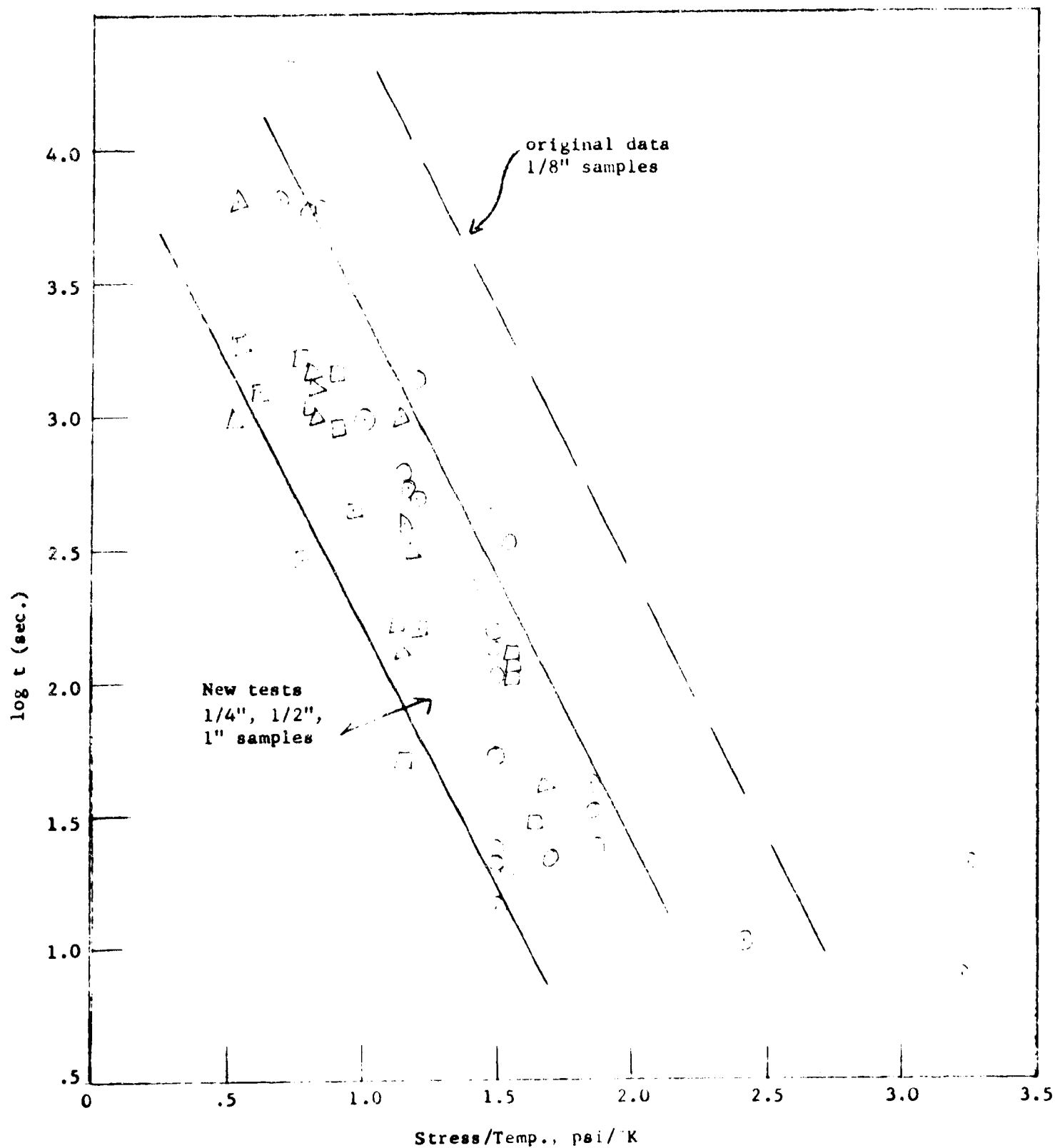SBR TREAD STOCKS TREATED WITH BENZENE

Figure 1

Inspection of these data show that the experimental
results exhibit the same general dependence of failure on stress for
all sizes of samples. There is no influence of sample size. The
apparent greater effectiveness of benzene in reducing failure times
of the larger samples could be attributed to many probable factors and
at present the cause of the scattering is not known. Further work on
test techniques will be planned as work progresses. All test data are
tabulated in Appendix A.

## Dynamic Testing with Cracking Agent Application

Static type testing has been the only method used
to demonstrate the failure characteristics of untreated and treated
tread stock samples in this program. In many service conditions,
the material fails from the action of small dynamically imposed strains
which cause stress patterns in the body of the material. These dynam-
ically stressed samples develop breaks, holes or tears which under
repetitive dynamically applied strain will produce complete mechanical
failure of the material. Some materials fail very rapidly under dynamic
conditions but show long useful life at equivalent or in more severe
static states. Since no information was available on the action of
cracking agents when used under dynamic conditions, some preliminary
experiments were run using the cut growth test[3] that was developed
as a dynamic test for evaluating the flex resistance of grooves in
tread stocks.

The cut-growth test is an accelerated procedure
used in the modified DeMattia machine[4] The test specimen is shown
in Figure 2. The on-inch-wide samples are cut from a molded slab
6 x 3 x 0.375 inches which has a U-shaped groove 0.187 inch deep
molded in the slab. Prior to testing, the center of the groove is
pierced through with a needle 0.037 inch in diameter. This initiates
a cut. The samples are held in a fixed lower jaw and a hinged upper
jaw by flat clamps in a position such that the upper section rotates
through an arc of a circle with a center just below the U-shaped
groove in the sample. Repeated flexure of the upper jaw alternately
stretches and closes the grooved region. Standard test conditions
are bending from 0° to 85° angular movement of the upper jaw at a
rate of 287 cycles per minute until the cut develops in the sample
to 0.5 inch in length. An automatic counter records the number of
machine flexes. The operator measures the width of the cut to the
nearest 0.01 inch and when the length of the cut approaches or exceeds
0.500 inch the test is considered complete. Results are reported as
kilocycles/inch to failure. This result is computed by linear extrapo-
lation of the kilocycle reading in terms of the fractional inch length
of the cut as measured at the final reading. This linear extrapolation
was found to be a reasonable assumption for most work.

The same conditions, described above, were used to
establish the kilocycles/inch to failure for untreated test specimens
for the SBR tread, SBR sidewall and Butyl tread stocks used in previous
static testing. Tests were run with three cracking agent treatments

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CUT-GROWTH TEST PIECE

Dimensions on molded test piece for
cut-growth test.

SPECIMEN

Figure 2
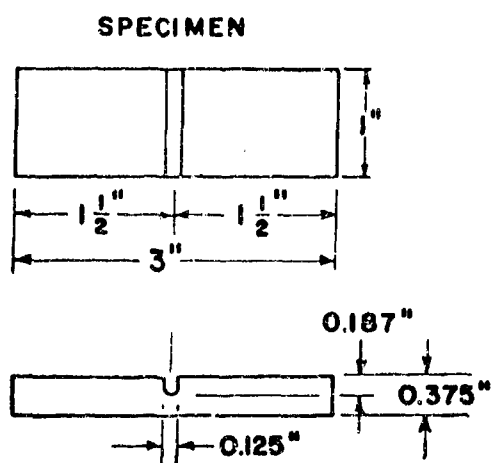
on each of the three stocks. Cotton swabs held in the groove by
strings lightly tied around the sample were saturated with the liquid
cracking agents at the start of the test for the treated specimens.
Test results shown in Table I compare the kilocycles/inch to failure
for untreated and treated tests. These results are the averages of
two samples for each test.

Table I

Dynamic Testing for Comparison of Cracking Agents

Stock	Kilocycles/inch to cut-growth failure			
	Untreated	Trichloroethylene	Decyl Alcohol	Benzene
SBR tread	280	21.5	8.8	16.2
SBR sidewall	703	12.0	32.0	6.4
Butyl tread	3330	6.0	19.0	11.0

These dynamic test data clearly demonstrate that
cracking agents promote failure under dynamic conditions. The relative
magnitude of the enhancement of the failure process is of the order of
100:1 for this form of dynamic testing as compared to the magnitude of
10^6 to 10^7 for static stress rupture tests. The reason for this spread
is not known but an examination of test conditions reveals a big differ-
ence in stress concentration as cracking develops in each test method.

In static stress rupture tests as the crack develops
the effective cross-section of the sample decreases but since the
loading remains constant the stress increases. The interaction of
these features is usually stated in summary form that stress concentra-
tion increases as failure progresses in static stress rupture tests.
In the dynamic flexure or bending test, the strain or extension is
fixed. Assuming that properties such as the modulus remain unchanged,
the tension stress at the s face of the groove is, for the simplified
case idealized to a beam problem, a function of the cross-sectional
dimensions. Now, a a crack develops, the cross-section dimensions
decrease and the force eeded to bend the beam to the same strain is
reduced. This interaction can be stated as the stress concentration
decreases in the cut-growth dynamic est as the cracking progresses.
The converse effects of stress concentration as cracking proceeds in
these static and dynamic tests would not be expected to exhibit identi-
cal changes in the progress of the failure mechanism and it would be
anticipated that the constant strain dynamic flexure test would show
a lower effectiveness of cracking agents than the static stress rupture
test. There are very likely other factors that influence these test
methods and further work in these areas will be scheduled. All test
data are listed in Appendix A.

Material Parameter Changes

General

Earlier work[1] demonstrated that the dependence of
stress rupture failure time on stress and temperature could be analyti-
cally described by an equation based on the failure mechanism proceeding
as a reaction rate process. Subsequent work[5] showed that the activation

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energy of the failure process may be considered as the energy for inter-
molecular separation. Stress rupture failure times over a range of stress
and temperature were measured for untreated materials to establish the
three material parameters for the equation relating stress, temperature
and failure time. Corresponding test work is underway to measure the
material parameters on specimens treated with cracking agents. Differ-
ences in material parameters from untreated and treated specimens and
within types of treatment are under examination for relations in terms
of the physical properties of the cracking agents and any interaction
between these treatments and the specimens.

<center>Comparison of Material Parameters for Normal and
Treated SBR Tread, Butyl Tread and Polyethylene</center>

Experimental work has been completed on the stress
rupture life for decyl alcohol treated samples of Butyl tire stock and
Marlex 6050 polyethylene at 200°K (81°F) and 339°K (150°F). In Table
II the material parameters as calculated from stress rupture data are
compared for normal and decyl alcohol treated SBR tread, Butyl tread
and polyethylene (Marlex 6050). Similar data on the SBR sidewall stock
is being rechecked to reduce some erratic trends. The decyl alcohol
treatment was used since it has a sufficiently low vapor pressure to
permit testing at temperatures above room temperature as required for
activation energy determination. All decyl alcohol treated specimens
showed reduced stress rupture failure times when compared with normal
specimens at the same test conditions. The new data shown in Table
II are results on treated Butyl tread and polyethylene and are presented
in Appendix A. All other results have been reported.

<center>Table II</center>

<center>Effect of Cracking Agent on Material Parameters</center>

<center>Decyl alcohol is cracking agent.</center>

	Act. Energy ΔF, kcal/mol		Element. Vol. $(\lambda q) \times 10^{24}$ cm^3		Freq. Factor Log N	
	Normal	Treat.	Normal	Treat.	Normal	Treat.
SBR Tread	25.5	19.7	7,330	7,060	4.54	6.20
Butyl Tread	44.8	56.0	11,320	11,320	-9.5	-17.5
Polyethylene (Marlex 6050)	37.8	27.6	5,800	5,800	-4.89	.39

The results listed in Table II reveal that the activa-
tion energy and the frequency factor are the two material constants
changed by cracking agent treatment of stress rupture tests. Experi-
ments have shown that there is only very minor changes in the elemental
volume value for these three materials and for the Butyl tread and poly-
ethylene this material parameter was taken as identical in value for
both normal and treated tests But SBR tread and polyethylene show a
reduction in activation energy due to treatment while Butyl tread shows

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shows an increase. This effect in Butyl tread may be some additional interaction that enhances the effect of decyl alcohol on this Butyl tread. The frequency factor exhibits a moderate increase for SBR tread and polyethylene but shows a large decrease for the Butyl tread. Explanations of these changes are being sought as shown by other work presented in this and previous reports.

Cracking Agents on Butyl Tread Stock

Characterization of the stress rupture tests on Butyl tread stock by the material parameters was given in Table II above. The Butyl tread was selected to observe the effect of different polymers on stress rupture properties. In addition to untreated tests, a group of tests are being made to determine whether the type of elastomer in the tread stock will influence the type of chemical structure in the cracking agent. Some of the results on these cracking tests are now becoming available for consideration.

Figure 3 is a plot of the log of the failure time in seconds as a function of stress level at room temperature. Results from two treatments are shown, namely trichloroethylene and xylene, both of which show great effectiveness as cracking agents on this butyl tread. Extrapolation of the untreated stress isothermal to values of $S/T < 2$ clearly show that both of these cracking agents reduce the failure time by a magnitude greater than 10^7. This is somewhat greater than the approximate reduction of about 10^6 in failure times for SBR tread tests with these two cracking agents.

These test results provide the information that cracking agents will show some effectiveness over a range of polymers. Further work on the influence of type of polymer in the tread stock is under consideration. All test data are given in Appendix A.

Cracking Agents on Polyethylene

Evaluation of cracking agent effectiveness on polyethylene (Marlex 6050 is also underway. Test results of the failure times as a function of the stress level are given in Figure 4 for xylene and nitrobenzene. Neither of these liquids appear to be very effective as cracking agents. The test data are listed in Appendix A.

Exploratory work was started to determine whether parameters such as the surface tension of the cracking agent is any indication of how effectively the liquid performed as a cracking agent. Room temperature stress rupture tests were run on 1/8" polyethylene samples with fourteen liquids to observe any trend of cracking behavior correlated with other properties of the cracking agents. The stress level chosen was 2140 psi which gave a S/T value of 7.1. This high level was selected in order to compare recent results with data tested earlier. Only single tests were made on each cracking agent. In Table III the failure times are listed in increasing order. Published values of the solubility parameters and surface tensions are listed to depict any trends in the data.

EFFECT OF CRACKING AGENTS ON THE STRESS RUPTURE LIFE OF

BUTYL TREAD STOCK
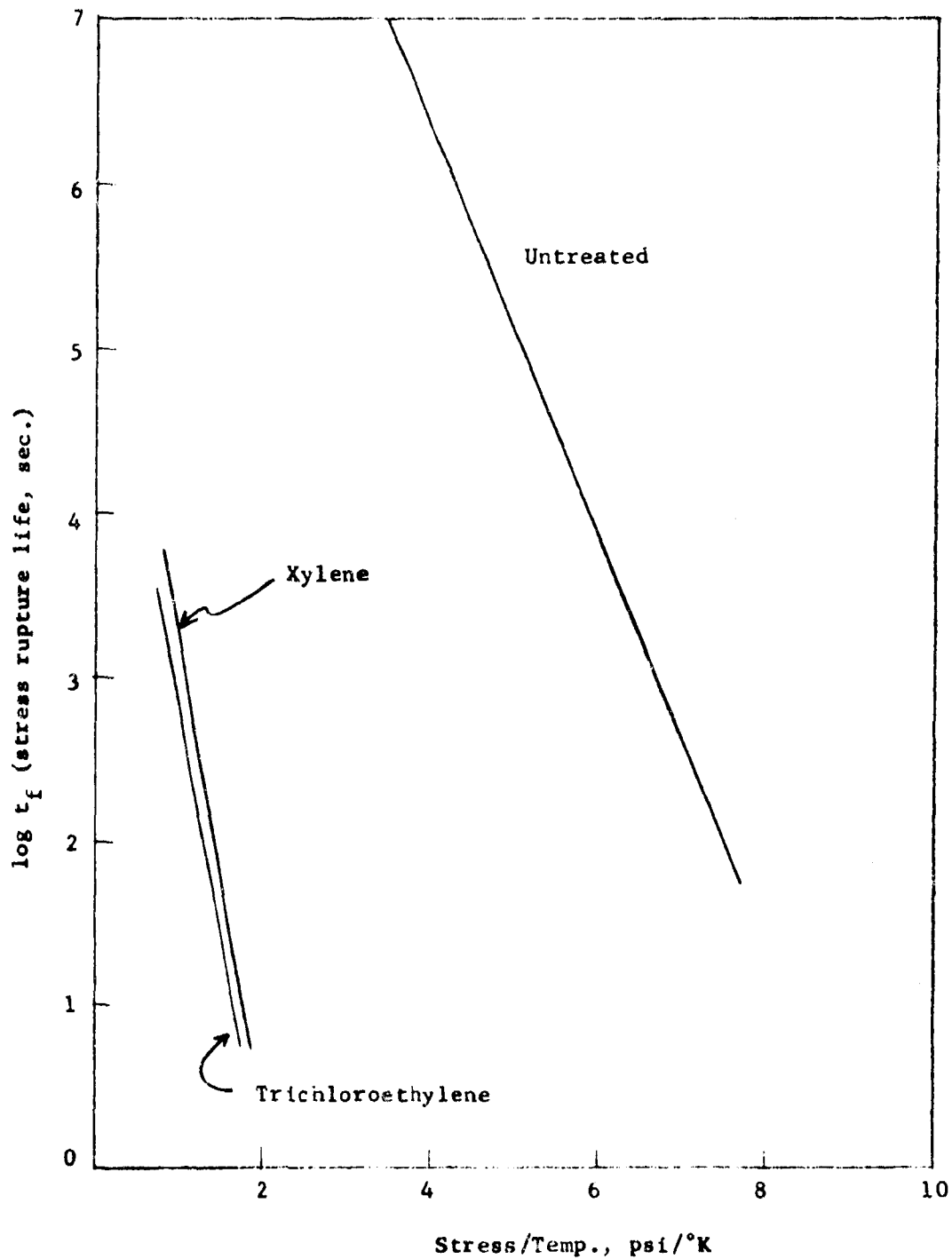
Tested at 27°C
Standard 1/8" samples

Figure 3

EFFECT OF CRACKING AGENTS ON THE STRESS RUPTURE LIFE

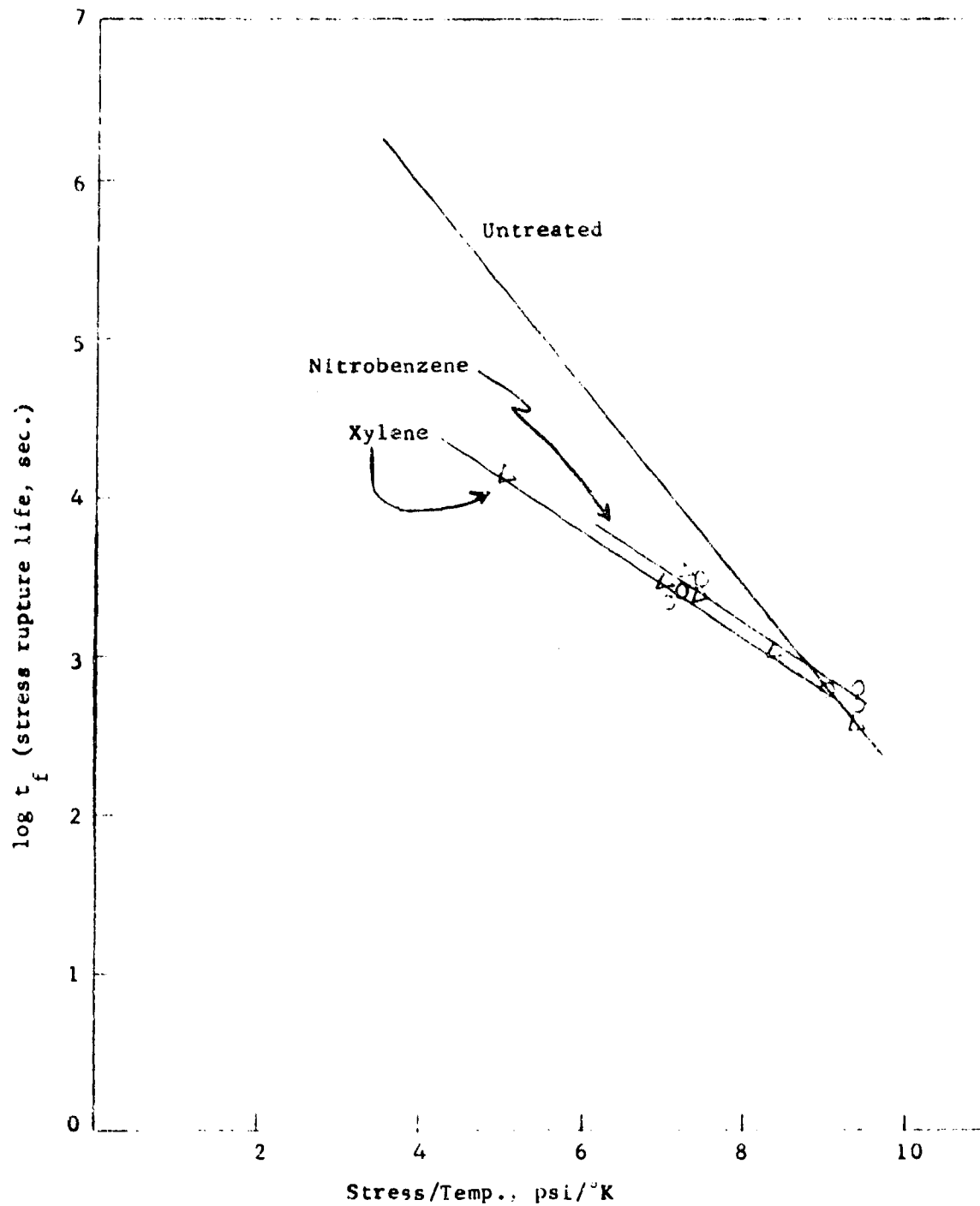OF MARLEX 6050 POLYETHYLENE

Tested at 27°C
Standard 1/8" samples

Figure 4

Table III

Failure Times of Polyethylene as Related to Solubility
Parameter and Surface Tension of Cracking Agents

Cracking Agent	Failure Time	Solubility Parameter	Surface Tension dyne/cm
nitrobenzene	1,910	10.0	43.9
xylene	2,210	8.8	29.0
bromoform	4,370	10.6	41.5
bromobenzene	4,380	10.2	36.5
hexane	4,550	7.3	18.4
methyl ethyl ketone	4,740	9.3	24.6
chlorobenzene	6,400	9.5	33.6
tetralin	6,436	9.5	-
turpentine	7,070	8.1	-
ethylene glycol	7,810	14.2	47.7
benzene	10,570	9.2	29
chloroform	10,740	9.3	-
methyl alcohol	> 13,300	14.5	22.6
glycerine	> 17,960	16.5	63
no treatment	11,000	-	-

Inspection of these results reveal only a small trend for solubility
parameter and practically no trend with surface tension with respect
to failure time. A careful study shows that as the halogen substituent
changes on either a single carbon (methyl) or aromatic group the crack-
ing effectiveness increases. This trend is under further study.

A Measure of Cracking Agent Efficiency

The effectiveness of a cracking agent in decreasing
the failure time of stress rupture samples can be measured by the shift
towards the origin of the stress isothermal for the treated tests as
compared with the untreated tests. This, however, necessitates testing
over a range of stress levels to establish the position of the stress
isothermal.

Exploratory work was started to determine whether
a somewhat simpler test could be used for quantitative evaluation of
the cracking effectiveness. It was suggested that the effectiveness
of a cracking agent be defined as the average of the logarithm of the
failure time for ten treated 1/8" samples tested at a stress level of
230 psi, each sample to be punctured with a .034" diameter needle.
The puncture was to initiate a crack or cut and thus reduce any induc-
tion period before cracking starts. Presumably the needle puncture
would reduce the scatter in failure times at lower stress levels, some
of which has been attributed to surface cuts on the sample.

A group of eight cracking agents was selected and
ten samples of SBR tread were tested on each cracking agent under the
conditions given above. The average of the $\log t_f$ for 10 samples
and the % average deviation is reported in Table IV. Improvement in
cracking effectiveness means a lowering in $\log t_f$, hence the lower
values of $\log t_f$ indicate a more effective cracking agent.

Table IV

Effectiveness of Cracking Agents

Averaged failure time of punctured samples used as measure of effectiveness.

Cracking Agent		Cracking time effectiveness	Averaged deviation $\pm$ %
methylene chloride	CH_2Cl_2	2.194	16.7
ethylene chloride	C_2H_4ClBr	2.594	16.0
chlorobenzene	C_6H_5Cl	2.640	10.0
trichloroethylene	$C_2H_5Cl_3$	2.674	8.2
chloroform	$CHCl_3$	2.705	9.7
benzene	C_6H_6	2.945	6.2
cyclohexane	C_6H_{12}	3.196	6.0
decyl alcohol	$C_{10}H_{21}OH$	no breaks (1 day)	-

The results listed above give a quantitative measure of effectiveness.

The breaking times varied from 2 minutes to 40 minutes with the exception of samples treated with decyl alcohol which did not fail under eight hours. Although decyl alcohol is a cracking agent, it is not as effective as any of the remaining seven liquids listed in the table. These results show that the halogen substituted hydrocarbons are more effective as cracking agents than the pure hydrocarbons. The spread between the most and least effective of the cracking agents is just one order of magnitude. The per cent averaged deviation decreases as effectiveness decreases and the overall averaged deviation is around $\pm$10% which is considered relatively small scattering in life test data. The use of this test measure is under consideration for future work. All test data are presented in Appendix A.

Part II

Properties of Importance in the Failure Process

General

Analysis of stress rupture failure data in terms of the reaction rate equation yields three parameters of the material. Since these parameters characterize the failure process over the range of stress and temperature used for testing, they are called the material parameters. Earlier work[5] directed towards identifying whether any physical properties were related to these three material parameters indicated that the activation energy of stress rupture failure, ΔF, was directly related to the cohesive energy of the material.

The importance of relating the material parameters with other properties arises from the need of determining how the failure process changes with physical properties. The introduction of surface properties is recognition that the cracking agents first contact the surface of the material and the action of cracking agents begins at the surface. Since there is no apparent chemical change on the stressed surface, the conclusion drawn is that the activity of cracking agents in accelerating the failure of a material is a physical change corresponding to a change of state in matter. Such changes involve secondary bonding forces that are of importance in determining the internal cohesive properties and the surface properties which are dependent on the molecular composition of the material.

Surface Energy of Polyethylene

In Report No. 3, pgs. 14-15, two methods were used for calculation of the surface energy of SBR tread stocks. Both methods evolved from the simplified ideal concept that the surface energy can be expressed by the general relation[6]

$$E_s = rE_v/3 \quad ergs/cm^2 \tag{1}$$

with E_s as the surface energy per unit area of a material composed of spherical particles with radius, r, and E_v is the unit volume energy or specific heat of vaporization. The spherical particles were considered equivalent to the material parameter, λq, from stress rupture data on the SBR tread stock. The heat of vaporization per unit volume is obtained from

$$E_v = \Delta H/V = \delta^2 + RT/V \quad cal/cm^3 \tag{2}$$

where δ is the solubility parameter from swelling tests on SBR tread, R is the gas constant, T is °K and V is the volume of a mole of the elemental units λq.

The second method of computing the surface energy was based on a corresponding concept with the relation

$$E_s = \delta^2 (V/N_o)^{1/3} \tag{3}$$

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where E_s and δ are the same as defined above but V is the molar volume estimated on the fractional volume contributions of the polymers in SBR tread (Report 2, pg. 15, eq. 7) and N_o is the Avagadro number. The two values of E_s for the SBR tread agreed within 15%.

The two methods described above have been used to calculate the surface energy of polyethylene (Marlex 6050). From Table I of this report the value of λq for polyethylene is 5800×10^{-24} cm^3 from which $r = 1.12 \times 10^{-7}$ cm. The published solubility parameter[7] for polyethylene is $\delta = 7.9$ and the computed value of E_v is 262×10^7 ergs/cm^3. Then from eq. (1) the surface energy is

$$E_s = .333 \times 1.12 \times 10^{-7} \times 262 \times 10^7$$

$$E_s = 97 \text{ ergs/cm}^2 \tag{4}$$

For the second method using equation (3) the molecular volume $(V/No)^{1/3}$ is estimated from the volume per monomer of the polymer chain in a unit cell. With unit cell dimensions[8] of a 7.40, b = 4.93, c = 2.53 angstroms and three ethylene monomer units per unit cell, the volume per monomer unit is 30.6×10^{-24} cm^3. Then for equation (3) the surface energy is

$$E_s = (7.9)^2 \times 4.17 \times 10^7 (30.6 \times 10^{-24})^{1/3}$$

$$E_s = 81.3 \text{ ergs/cm}^2 \tag{5}$$

These two computed surface energies show about 12% difference which is about the same variation observed for the SBR computation.

A precise evaluation of the surface energy of a liquid can be made by subjecting the surface to a thermodynamic cycle[6] which gives

$$E_s = \gamma + T \, d \, \gamma/dT \tag{6}$$

where γ is the surface tension and T is the temperature. The slope of γ as a function of increasing temperature is negative since at the vaporization temperature $\gamma = 0$ and at temperatures less than vaporization the surface tension is positive. Values of the surface energy for polyethylene have been determined[9] and the temperature dependence[10] of the surface energy has also been evaluated at elevated temperatures. Entering corrected room temperature values in eq. (6) gives

$$E_s = 31 - 300 \, (-.076)$$

$$E_s = 53.8 \text{ ergs/cm}^2 \tag{7}$$

Although this result was calculated by treating the surface energy of polyethylene as a liquid, it is considered as a reasonable determination of the surface energy.

The need for improvement in the initial two methods of computing surface energies is apparent. The primary significance of these results is not the absolute numerical values but is the fact that material parameters measured in stress rupture failure testing do have an absolute relation with other recognized physical constants of the material.

The achievement of establishing the basic relations for the material parameters can be considered a fundamental development in this work, however, the potential usefulness of this concept will probably be of more value when used in the reversed direction. For example, if the material constants of stress rupture failure tests are correlated with molecular properties of the material, then it should be possible to calculate the material parameters of stress rupture tests from the known material properties provided that the equations correctly describe the inter-relations. This is easily demonstrated by recalling that the surface energy (Report #2, p. 14, eq. 1) required to separate the elemental units was described as

$$E_s = (\Delta F/N_o)/(\lambda q)^{2/3} \tag{8}$$

which can be rearranged as

$$\Delta F = E_s N_o (\lambda q)^{2/3} \tag{9}$$

Now from eq. (7) and with $\lambda q = 5800$ cubic angstroms, the calculated activation energy is

$$\Delta F = 53.8 \times 6.02 \times 10^{23} (5800)^{2/3} \times 10^{-16}$$
$$\Delta F = 25 \text{ kcal/mole} \tag{10}$$

The value of ΔF (see Table I) for the polyethylene stress rupture tests is 38.3 kcal/mol. The activation energy calculated from surface tension data is about 66% of the measured value from stress rupture tests. Although this may appear to be a large error, it is, in fact, surprisingly small since there was no priori reason why the entire energy value of the activation energy should arise solely from the molecular forces as measured by surface energy experiments. This initial crude evaluation shows that almost 2/3 of the activation energy can be accounted for by intermolecular forces that can be measured by the surface energy of a material.

The establishment of these guide lines for evaluation of material parameters from the physical properties that govern the changes in the material parameters is being used for estimating what types of cracking agents should be examined in future work. Some preliminary work along these lines is described in the following sections.

Surface Tension of Binary Mixtures

The application of a cracking agent to the stressed surface of a polymer is considered to produce some type of interaction at the surface which promotes or increases the failure process. A study is being made to determine whether this interaction can be treated as a binary system with a surface tension evaluated on the basis of ideal solutions.

The surface tension of a binary solution[11] is given as:

$$\gamma_{12} = x_1\gamma_1 + x_2\gamma_2 - \frac{\Sigma}{2RT}(\gamma_1-\gamma_2)^2 x_1 x_2 - \cdots \qquad (11)$$

where γ_1 and γ_2 are the surface tensions of x_1 and x_2 mole fractions at the interface of the two components, R is the gas constant, T is absolute temperature and Σ is the surface area per mole based on the assumption that both components have equivalent surface areas, i.e. $\Sigma = \Sigma_1 = \Sigma_2$. To calculate the surface energy E_s, the thermal dependence of γ or $d\gamma/dT$ is required. Differentiating eq. (11) yields

$$\frac{d\gamma_{12}}{dT} = \frac{x_1 d\gamma_1}{dT} + \frac{x_2 d\gamma_2}{dT} - \frac{x_1 x_2 \Sigma}{2R}\left[\frac{2(\gamma_1-\gamma_2)}{T}\left\{\frac{d\gamma_1}{dT} - \frac{d\gamma_2}{dT}\right\} - \left(\frac{\gamma_1\gamma_2}{T}\right)^2\right] + \cdots \qquad (12)$$

The third term in eq. (11) is numerically much smaller than the first two terms for most organic liquids and eq. (11) can be simplified to

$$\gamma_{12} = x_1\gamma_1 + x_2\gamma_2 \qquad (13)$$

and for similar reasons eq. (12) may be written as

$$\frac{d\gamma_{12}}{dT} = \frac{x_1 d\gamma_1}{dT} + \frac{x_2 d\gamma_2}{dT} \qquad (14)$$

The surface energy for the binary solution mixture is

$$E_{s12} = \gamma_{12} + Td\gamma_{12}/dT \qquad (15)$$

and inserting the appropriate quantities from eqs. (13) and (14) gives

$$E_{s12} = x_1(\gamma_1 + Td\gamma_1/dT) + x_2(\gamma_2 + Td\gamma_2/dT) \qquad (16)$$

or

$$E_{s12} = x_1 E_{s1} + x_2 E_{s2} \qquad (17)$$

which shows for this simplified ideal case that the effective surface energy of the binary mixture is an additive property of the molar fractions

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of each component. From eq. (17) the prediction can be made that if one component has a high surface energy and the other component a lower surface energy, then the surface energy of the binary mixture will be an intermediate value between these two limits and will be proportional to the relative concentrations present.

The idealized version presented above utilized simplifications and assumptions that are not met in practical work. As a check on the accuracy obtained with the classical concepts and to illustrate the method, some calculations of the surface tension have been made and the results are compared with published values[12] of binary solutions.

Example 1. Binary mixture of acetone (78.17% and diethyl ether (21.83%) at 20°C) per cent by weight). There are .742 mols of acetone (component 1) and 3.4 mols of diethyl ether (component 2) which give $x_1 = .179$ and $x_2 = .821$. To evaluate Σ, the values for Σ_1 and Σ_2 are computed and averaged.

$$\Sigma_1 = (N_o V)^{1/3} = 1.49 \times 10^9 \text{ cm}^2/\text{mol}$$

$$\Sigma_2 = 1.86 \times 10^9 \text{ cm}^2/\text{mol}$$

with an average of $\Sigma = 1.66 \times 10^9$ cm^2/mol, then substituting in eq. 11

$$\gamma_{12} = .179 \times 23.7 + .821 \times 17.01 - \frac{1.66 \times 10^9}{1.98 \times 600} (23.7-17.01)^2 (.179 \times .820)$$

or

$$\gamma_{12} = 4.24 + 13.95 - .22 = 17.97 \text{ dyne/cm.}$$

The measured value of surface tension reported for this binary system is 16.75 dyne/cm or a difference of 7.3%. If the third term of the calculation was neglected, the error would be 8.6% of the measured value.

Example 2. Binary mixture of acetonitrile (89.17%) and ethanol (10.83%) at 20°C (percentage by wt.). Computations for this system yield $x_1 = .125$, $x_2 = .875$, $\Sigma_1 = 1.38 \times 10^9$ cm^2/mol, $\Sigma_2 = 1.25 \times 10^9$ cm^2/mol, $\Sigma = 1.31 \times 10^9$ cm^2/mol.

$$\gamma_{12} = 3.66 + 23.3 - .0223 = 26.94 \text{ dyne/cm}$$

Measured values are $\gamma_1 = 29.3$, $\gamma_2 = 26.58$, $\gamma_{12} = 22.92$ dyne/cm. Computed value of γ_{12} is 17.5% higher with the third term and 17.6% without this term.

Example 3. Binary mixture of carbon tetrachloride (69.60%) and benzene (30.40%) at 50°C (per cent by wt.). This yields $x_1 = 458$, $x_2 = .542$, $\Sigma = 1.71 \times 10^9$ cm^2/mol and

$$\gamma_{12} = 10.7 + 13.4 - .0147 = 24.09 \text{ dyne/cm.}$$

Measured values are $\gamma_1 = 23.38$, $\gamma_2 = 24.74$, $\gamma_{12} = 24.39$ dynes/cm. The computed value differs from the measured by 1.23% with the third term and 1.19% without this term.

These results show excellent to good agreement between computed and measured values of surface tension for binary liquid mixtures. The simplified version eq. (13) gives values that are satisfactory for most evaluations.

Surface Energies of Binary Solvent Systems

In a recent paper Meltzer[13] presented work on the swelling of a SBR vulcanizate as related to the solubility parameter δ of binary solvent systems. The SBR stock was vulcanized with 16% sulfur. The solubility parameters of the binary solvent systems were varied by adjusting the components of the mixture in accordance with the Small[11] relation

$$\delta = \frac{x_1 V_1 \delta_1 + x_2 V_2 \delta_2}{x_1 V_1 + x_2 V_2} \tag{18}$$

where x_1, x_2 are the mol fractions, V_1, V_2 are molar volumes and δ_1, δ_2 are the solubility parameters.

From Meltzer's plot of present volume swelling as a function of δ, the value of δ at maximum swelling can be estimated. Entering this on the left hand side of eq. (18) and also appropriate values for molar volumes and solubility parameters of each component, eq. (18) can be solved for the ratio of mol fractions for the components. Using an arbitrary weight of one component, the computed mol fraction ratio establishes the weight of the other component and the surface tension of the binary solvent system for maximum swelling can be computed by eq. (13). The surface entropy term can be evaluated from published values of $d\gamma/dT$ for each solvent which are entered in eq. (14). The surface energy for maximum swelling is calculated from eq. (16).

As an example the surface energy for the binary system n-octane/ethanol at 60°C will be computed. For this system maximum swelling of 15% occurs at $\delta = 9.5$. Then after entering molar volumes and solubility parameters for these two solvents in eq. (18), the result is

$$9.5 = \frac{x_1 (16.2) \ (7.6) + x_2 \ (57.5) \ (12.7)}{x_1 \ 16.2 + x_2 \ 57.5}$$

Solving for x_1, x_2 gives

$$x_1 = 0.66 \ x_2 \tag{19}$$

Now for a mixture of, say, 10 gm. of ethanol, the mol fractions are $x_1 = .397$ $x_2 = .603$.

The surface tension for this binary system at maximum swelling can be calculated from eq. (13) as

$$\gamma = (.397)(18.6) + (.603)(18.9) = 18.78 \ \text{dyne/cm.} \tag{20}$$

The surface entropies $d\gamma/dT$ from published values[12] are $d\gamma_1/dT = .0814$ dyne/cm and $d\gamma_2/dT = .0854$ dyne/cm. Then with eq. (16) the surface tension is

$$E_{s12} = .397 [18.6 + 333 (.0814)] + .603 [18.9 + 333 (.0854)]$$

$$E_{s12} = 46.7 \text{ ergs/cm}^2 \tag{21}$$

Similar calculations were performed for systems of aceto-nitrile/toluene and ether/cyclohexanol and the results are given in Table V. In this table, the computed surface energy of the binary mixtures at the same solubility parameter level as that at which maximum volume swelling was obtained are arranged in order of decreasing solubility parameter.

Table V

Computed Surface Energy for Maximum Swelling

| Binary Mixtures | Solubility Parameter | Computed Values | | | % Maximum Vol. Swell |
		Surface Tension	Surface Entropy	Surface Energy	
n-octane/ethanol	9.5*	18.78	.0838	46.70	15
diethyl ether/ cyclohexanol	9.2*	20.30	.115	58.60	42
acetonitrile/toluene	8.9*	23.60	.115	61.90	90
benzene/toluene	9.0	28.66	.123	65.52	-

* from Meltzer's paper.

The benzene/toluene result was added for comparison since this system was one of the best cracking agents found in earlier testing on SBR tread (Report No. 3, pgs. 13 and 26).

The surface energies increase with maximum volume swelling for this highly vulcanized SBR compound of Meltzer's work. Also, the surface energies show a greater spread than the solubility parameters which indicates that E_s is a more sensitive indicator of the influence of the solvent mixtures. The overall purpose of this comparison confirms a hypothesis that surface energy is a more discriminating property of cracking agents than the solubility parameter and that the extension of techniques for understanding the influence of surface proper-ties will yield information on the mechanism of cracking agents.

Spreading Coefficient of a Liquid on a Solid

The concept that the stability of a drop of liquid on the surface of a solid was a system in static equilibrium between the interfaces of the liquid, solid and vapor around the liquid was origi-nated by Thomas Young.[15] The conventional equation for the balance of forces is given by the surface tension relation

$$\gamma_{sv} - \gamma_{sL} = \gamma_{Lv} \cos \theta \tag{22}$$

where the subscripts refer to solid-vapor, solid liquid and liquid vapor. The angle θ is the contact angle of the liquid drop and the solid as indicated in the diagram at the right. This angle can be measured for a system in thermodynamic equilibrium.
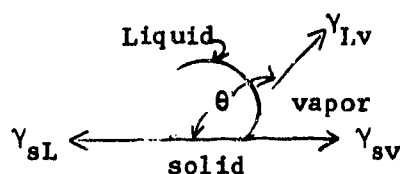
Further developments[16] from these concepts had led to the conditions for the spreading of a substance b on another material a in terms of a relation

$$S = \gamma_a - (\gamma_b + \gamma_{ab}) \tag{23}$$

where spreading occurs for $S > 0$ and conversely non-spreading when $S < 0$. For a liquid-solid system eq. (20) becomes

$$S = \gamma_s - (\gamma_{Lv} + \gamma_{sL}) \tag{24}$$

This relation can be simplified further by making use of the fact[17] that γ_{sL} is usually much smaller than γ_{Lv} which gives the approximation

$$S \cong \gamma_s - \gamma_{Lv} \tag{25}$$

Since most solids have a relatively high surface tension compared to liquids in equilibrium with their vapor, most liquids wet or spread on solids for S will be greater than zero. However, for organic solids such as polymeric materials the surface tension is in the same range as the surface tension of many organic liquids. As a consequence many liquids will not spread on organic solids. Incidentally, the use of eq. (24) cannot be applied without caution; however with organic substances where polarity or other effects are not of importance, the approximation is in reasonable agreement with experimental evidence.

Application of this technique has been made to obtain an estimate of the surface tension of the elastomer stocks used in our work. A series of organic liquids were selected with a range of γ_{Lv} and visual observation was used to detect spreading on the surface of the stock. The results are listed in Table VI.

Table VI

Spreading of Organic Liquids on Elastomer Stocks

Liquid	γ_L	S(SBR Tc)	S(SBR SW)	S(Butyl)
iso-pentane	13.72	+	+	+
ethyl ether	17.01	+	+	+
n-hexane	18.43	+	+	+
heptane	21.19	+	+	+
n-octane	21.8	+	+	+
ethyl alcohol	22.75	-	-	-
acetone	23.70	-	-	-
methyl ethyl ketone	24.6	-	-	-
cyclohexane	25.5	-	-	-
methylene chloride	26.52	-	-	-
carbon tetrachloride	26.95	-	-	-
chloroform	27.14	-	-	-
toluene	28.5	-	-	-
benzene	28.85	-	-	-
o-xylene	30.10	-	-	-
nitro ethane	32.2	-	-	-
tetrachloro ethane	33.09	-	-	-
chlorobenzene	33.56	-	-	-
dioxane	35.23	-	-	-
nitrobenzene	43.9	-	-	-

S > 0 indicates spreading (+)

S < 0 indicates non-spreading (-)

Inspection of the data reveals that the spreading ceases for all three stocks when the surface tension of the liquid is greater than γ = 22 dyne/cm. A very interesting point about these data is that the liquids that have exhibited excellent cracking behavior such as tetrachlorethane, benzene, toluene, chloroform and others do not spread on the polymer stocks tested. The meaning of this observation is not clear and further work to better understand this point is being planned.

Surface Tensions of Polymers

In a previous report a calculated estimate of the surface tension for the SBR tread stock was attempted by using an empirical relation found acceptable for organic liquids with approximations for the elastomer solubility parameter and molar volumes. The value obtained was 28.9 dyne/cm. (Report 3, pgs. 15, 16).

For the purpose of assessing whether this determination was a reasonable value, published data[9] on surface tensions and solubility parameters were compared. The surface tensions in this published work were estimated by the critical surface tension technique. Values of the surface tension are plotted as a function of the solubility parameter in Figure 5. Included on the plot is the surface tension value of 28.9 dyne/cm. for the SBR tread that was discussed above. It is evident that the

COMPARISON OF CRITICAL SURFACE TENSION AND SOLUBILITY

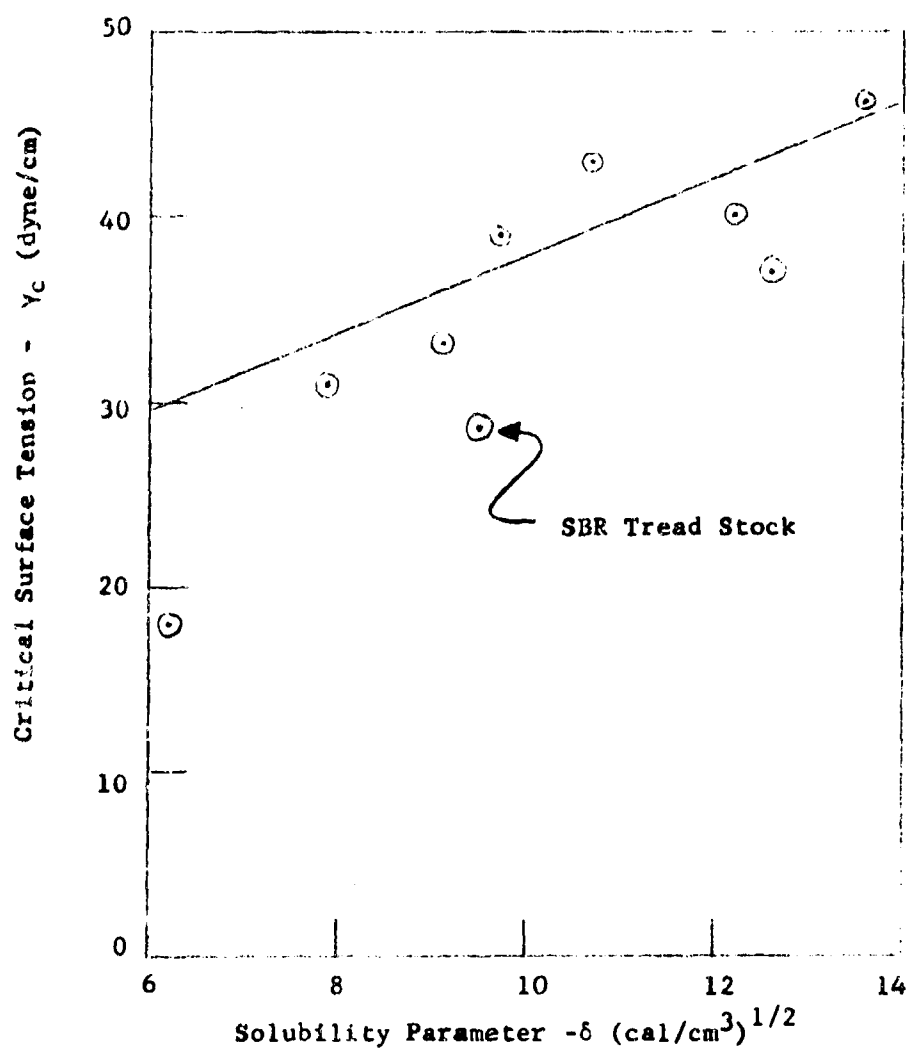## PARAMETER FOR POLYMERS

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Figure 5

SBR value is in good agreement with the other polymers. Although this agreement does not confirm the reliability of the method or approximations used in computing the surface tension estimate of SBR tread, the comparison is encouraging.

Cracking Agents with Substituents on Benzene Ring

Stress rupture test results from samples treated with various cracking agents have indicated that the type of molecular structure may be of importance in determining the effectiveness of the cracking agents. In work previously reported, the aromatic hydrocarbons appeared more effective than linear hydrocarbons. Also, there was some evidence that pointed towards an improvement in cracking when one or more polar type substituents were present on the carbons. These ideas suggested some additional exploratory tests on readily available chemicals.

A group of aromatic hydrocarbons with various substituents were used as cracking agents on SBR tread stock. The six aromatic types were nitrobenzene, chlorobenzene, o-dichlorobenzene, fluorobenzene, bromobenzene and tetrahydronaphthalene. These compounds represent a single or double substitution on previously tested cracking agents. The tetrahydronaphthalene is essentially a double benzene ring. In addition, bromoform was tested to compare with chloroform which was one of the more effective linear type cracking agents.

The stress rupture isothermals for the tests with the six aromatic compounds are shown in Figure 6. Included on the figure is a previously reported result for benzene. Also, for an aid in comparison, the coordinate point with value (2,2) is marked with an encircled cross to enable reference with other plots. These results do not show any large differences in cracking behavior. The slope change of the chlorobenzene tests appears unusual on this enlarged plot but no significance is attached to it.

Figure 7 is a similar plot with reduced coordinates that compares the cracking of bromoform with previous results for chloroform. Although here again there is an apparent slope change, the comparison with the reference point indicates no appreciable change. The vertical bar on each line is an indicator of the scatter in the tests.

These exploratory tests did not yield any production leads except to extend the number of agents that are effective in cracking SBR tread stocks. All test results are listed in Appendix B.

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EFFECT OF SUBSTITUTION ON BENZENE RING STRUCTURE ON STRESS

CRACKING OF SBR TREAD STOCK

All tests at °C

The circled cross is at reference point for a comparison guide.

Stress (psi)/Temp. (°K)
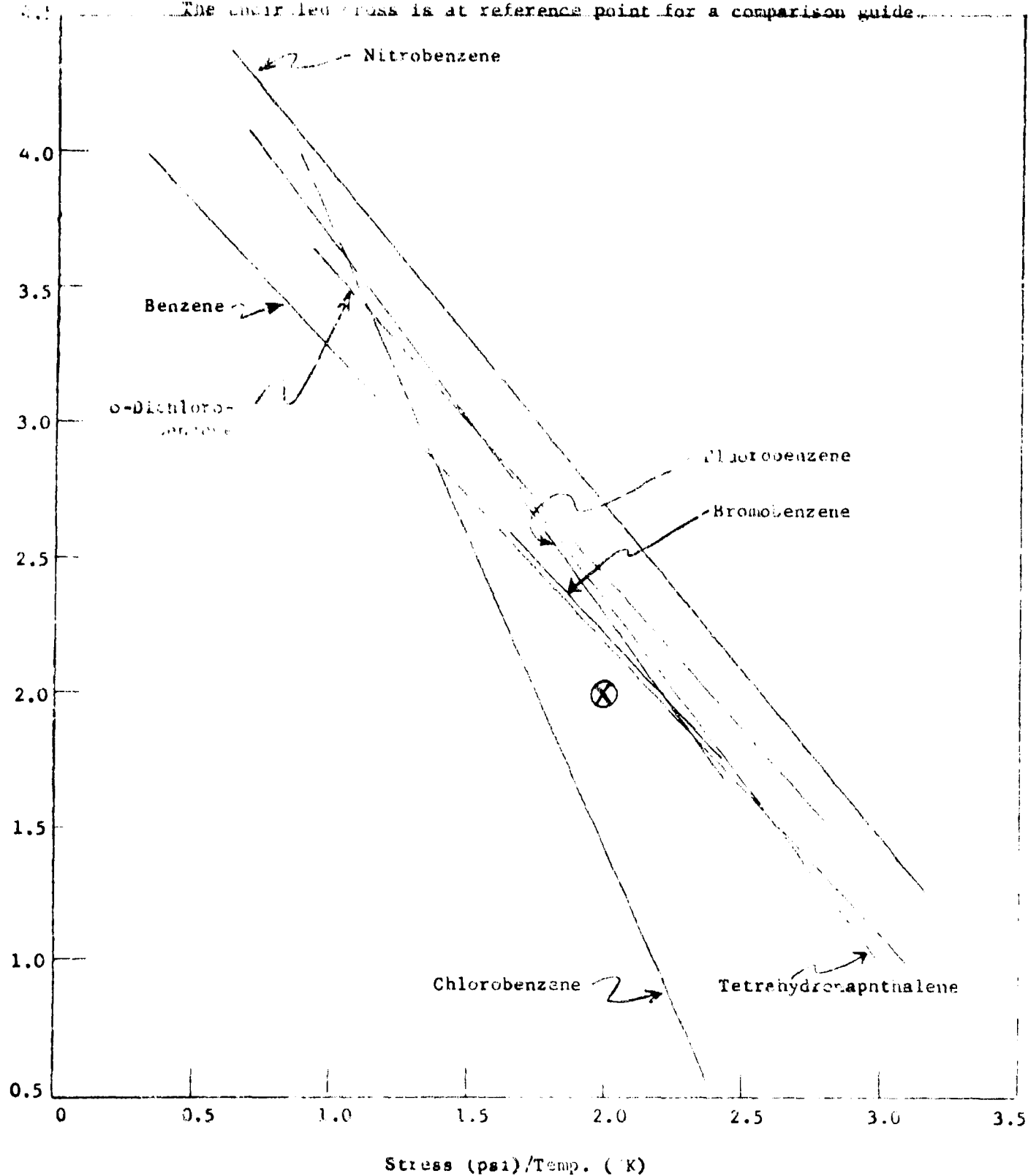
Figure 6

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COMPARISON OF CRACKING EFFICIENCY OF CHLOROFORM AND

BROMOFORM ON SBR TREAD STOCK

All tests at 27 C
The enclosed cross is a reference point for a comparison guide.

Stress (psi)/Temp. (°K)
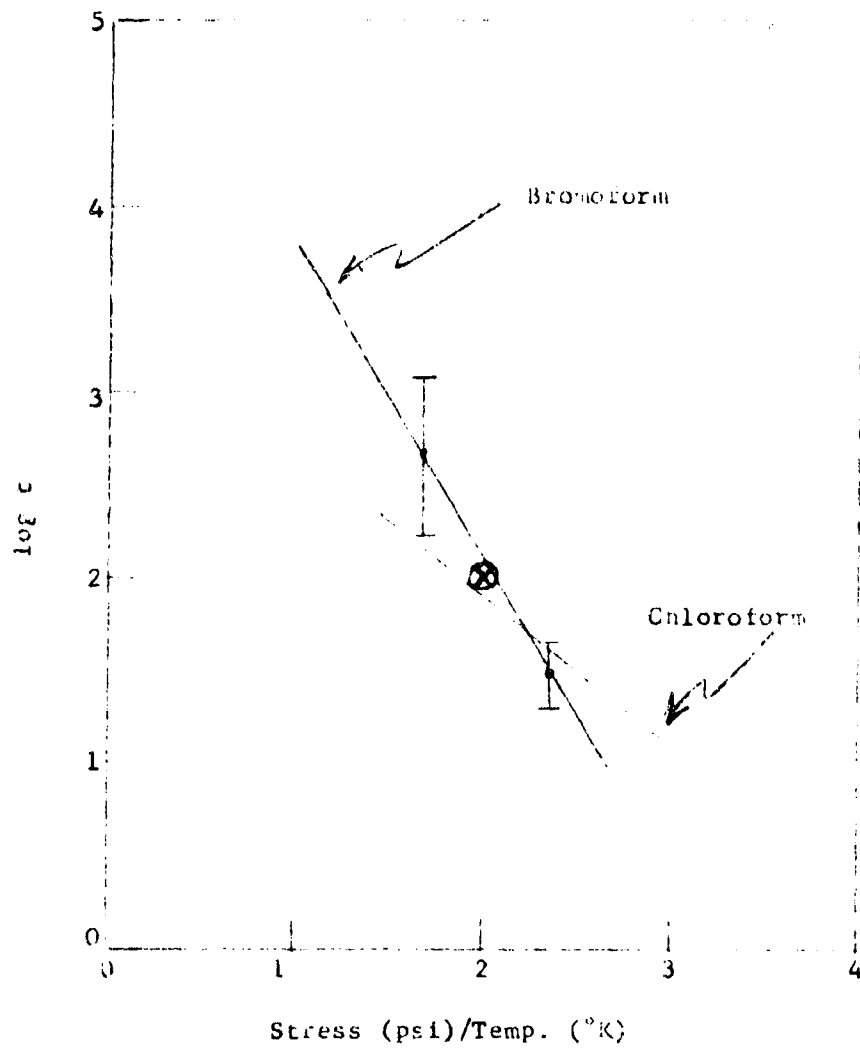
Figure 7

Summary and Conclusions

Results presented in this report cover the following work. Experiments have shown that failure time of treated samples is not influenced by sample size. Sets of material parameters for untreated and treated samples of SBR tread, Butyl tread and polyethylene have been obtained. Exploratory trials of cracking agents on Butyl tread produce a 10^7 reduction in failure time as was found for SBR tread. Cracking agents effective on tread stocks have little effect on polyethylene. An accelerated test for cracking effectiveness is being developed. Surface properties of polymers appear to have a specific influence in cracking effects. Computation of surface energy of polyethylene by three methods is in fair agreement and has established an important guideline in the mechanism of failure. Calculation methods for surface energies of binary mixtures was used to evaluate surface energy at maximum swelling of a vulcanized SBR stock. Experiments on spreading of organic liquids on SBR tread were used for an estimate of surface tension of the tread stock. Comparison of surface tension and solubility parameters of various polymers was made to show agreement with computed surface tension of SBR tread. Cracking tests with substituents on benzene ring are as effective as benzene.

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APPENDIX A

The contents of this appendix are discussed in Part I of this report.

Contents

Table A-1

Effect of Sample Size on Failure Time

Material:	SBR Tread Stock	
Conditions:	Benzene on Surface	
Temperature:	300°K (27°C)	

Sample Size	Stress (psi)	Failure Time (sec.)
1" (P/A = 27)	500	40
	353	300
	353	30
	344	406
	344	135
	344	979
	247	1100
	247	1308
	247	1467
	163	1880
	159	826
	159	2085
	159	6274
1/2" (P/A = 29)	488	29
	464	124
	464	116
	464	103
	362	161
	348	278
	343	51
	339	166
	289	429
	270	914
	270	1414
	238	1007
	232	286
	228	1617
	189	1197
1/4" (P/A = 33)	977	20
	967	7.5
	727	10.0
	562	23
	555	41
	555	33
	510	21
	463	328
	457	19
	452	21
	452	23
	452	52
	451	14
	451	108
	451	121

Sample Size	Stress (psi)	Failure Time (sec.)
1/4" (P/A = 33)	446	130
	417	218
	358	1232
	358	483
	348	532
	345	594
	302	931
	252	5551
	240	5760
	218	19292
	209	6487
1/8" (P/A = 41)	See Report No. 3, page 35	

Table A-II

Dynamic Cut Growth Tests on Treated Stocks

All tests at room temperature (25°C)
Conditions of test are described in text.

Stocks	Treatment	Kilocycles of Test	Cut Length, inches	Estimated failure, kc/inch
SBR tread	none	138.2	.50	276.4
		141.6	.50	283.2
	trichloroethylene	12.2	.52	23.4
		11.0	.56	19.6
	decyl alcohol	5.9	.66	8.9
		5.9	.68	8.6
	benzene	11.1	.58	19.1
		6.9	.52	13.2
SBR sidewall	none	309.3	.51	606.4
		399.6	.50	799.2
	trichloroethylene	3.9	.62	6.2
		10.7	.60	17.8
	decyl alcohol	17.0	.50	34.0
		15.7	.52	30.1
	benzene	3.8	.70	5.4
		4.6	.62	7.4
Butyl tread	none	400.0	.10	4000
		400.0	.15	2666
	trichloroethylene	9.9	.58	17.0
		2.9	.56	5.1
	decyl alcohol	11.5	.50	23.0
		9.5	.64	14.8
	benzene	6.9	.50	13.8
		5.9	.69	8.5

Table A-III

Stress Rupture Life of Butyl Tread Stock
at Two Temperatures
Conditions: Cracking agent on surface

Cracking Agent	Temperature	Stress psi	Time to Fail sec.	$\log t_f$
Decyl Alcohol	27°C	1518	5919	3.772
		1518	5510	3.742
		1551	11917	4.076
		1840	750	2.875
		1895	514	2.710
		1864	350	2.544
	66°C	885	157	2.196
		891	46	1.663
		885	112	2.049
		891	118	2.072
		469	7202	3.857
		474	1180	3.072
		488	1227	3.089
		379	9200	4.963
		379	10300	5.012

Date are plotted on Figure A-1

Table A-IV

Stress Rupture Life of Marlex 6050 Polyethylene with Cracking Agent on Surface

Cracking Agent	Temperature	Stress psi	Time to Fail sec.	$\log t_f$
Decyl Alcohol	$66°C$	1510	624	2.795
		1500	576	2.761
		1510	1068	3.028
		1035	3560	3.552
		1035	2880	3.460
		1035	4680	3.670
		553	21600	4.334
		558	23040	4.363

Table A-V

Stress Rupture Life of Butyl Tread Stock with
Various Cracking Agents on Surface

Cracking Agent	Temperature	Stress psi	Time to Fail sec.	Log t_f
Xylene	27°C	505	41	1.632
		492	9	.954
		512	18	1.255
		291	2811	3.448
		295	485	2.686
		295	881	2.945
Trichloro- ethylene	27°C	303	361	2.558
		303	871	2.940
		489	12	1.079
		489	12	1.079
		636	>5	

Table A-VI

Stress Rupture Life of Marlex 6050 Polyethylene with Cracking Agents on Surface

Cracking Agent	Temperature	Stress psi	Time to fail sec.	$\log t_f$
Xylene	27°C	2580	1010	3.040
		2100	2832	3.452
		2820	366	2.564
		2775	630	2.799
		2165	3296	3.518
		2240	2380	3.376
		1530	13339	4.126
		1510	14526	4.162
Nitrobenzene	27°C	2820	465	2.668
		2130	2136	3.329
		2720	589	2.770
		2820	595	2.774
		2175	2261	3.354
		2240	3019	3.479
		1526	12441	4.096
		2566	566	2.753
		2105	3411	3.533
Benzene	27°C	2605	1668	3.222
		2610	5900	3.77
		2710	4216	3.625
		2760	2141	3.33
		2170	10570	4.024
		2340	8800	3.946

Table A-VII

Effectiveness of Cracking Agents

Material: SBR Tread Stock
Conditions: Cracking agent on surface of 1/8" sample
punctured with .034" diameter needle
Temperature: 300°K (27°C)

Cracking Agent	Formula	Stress (psi)	Failure Time, sec.
Benzene	C_6H_6	230	596
		230	2365
		230	713
		230	703
		230	1060
		230	1487
		230	1467
		230	1783
		230	784
		230	1220
Cyclohexane	C_6H_{12}	233	968
		233	2154
		233	2264
		233	2386
		233	1242
		233	1460
		233	2510
		233	386
		233	2127
		233	2173
Trichloroethylene	C_2HCl_3	236	965
		236	549
		236	148
		236	896
		236	482
		236	427
		236	431
		236	318
		236	1295
		236	216
Chlorobenzene	C_6H_5Cl	239	664
		230	102
		228	548
		228	748
		228	619
		228	800
		228	490
		233	342
		233	1230
		233	88

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Cracking Agent	Formula	Stress (psi)	Failure Time, sec.
Chloroform	$CHCl_3$	230	188
		230	785
		230	1013
		230	561
		233	67
		233	600
		233	695
		233	930
		233	683
		233	746
Methylene Chloride	CH_2Cl_2	230	1133
		230	179
		230	46
		230	52
		230	48
		230	640
		228	112
		228	263
		228	108
		228	184
Ethylene Chloro-bromide	C_2H_4ClBr	230	1236
		230	80
		230	1485
		230	287
		230	1549
		230	60
		230	317
		230	184
		230	462
		230	850
Decyl Alcohol	$C_{10}H_{21}OH$	255	No break @14,500 sec.
		255	No break @14,500 sec.
		255	No break @14,500 sec.

COMPARISON OF UNTREATED AND TREATED ISOTHERMAL

STRESS RUPTURE LIFE OF BUTYL TREAD STOCK

Untreated samples tested in air.
Treated samples have decyl alcono... ..t
to stressed surtace.

Figure A-1

ANALYSIS OF STRESS RUPTURE LIFE OF BUTYL TREAD STOCK

UNTREATED AND TREATED WITH DECYL ALCOHOL

Arrhenius plot for evaluation of activation energy
and frequency factor.

Untreated

ΔF = 44.8 kcal/mol.
N = .33 $\times 10^{-8}$

Decyl Alcohol Treated

ΔF = 56 kcal/mol.
N = .3 $\times 10^{-16}$

$\log t_f \ (S/T = 0) + \log T$

$10^3/T, \ ^\circ K$
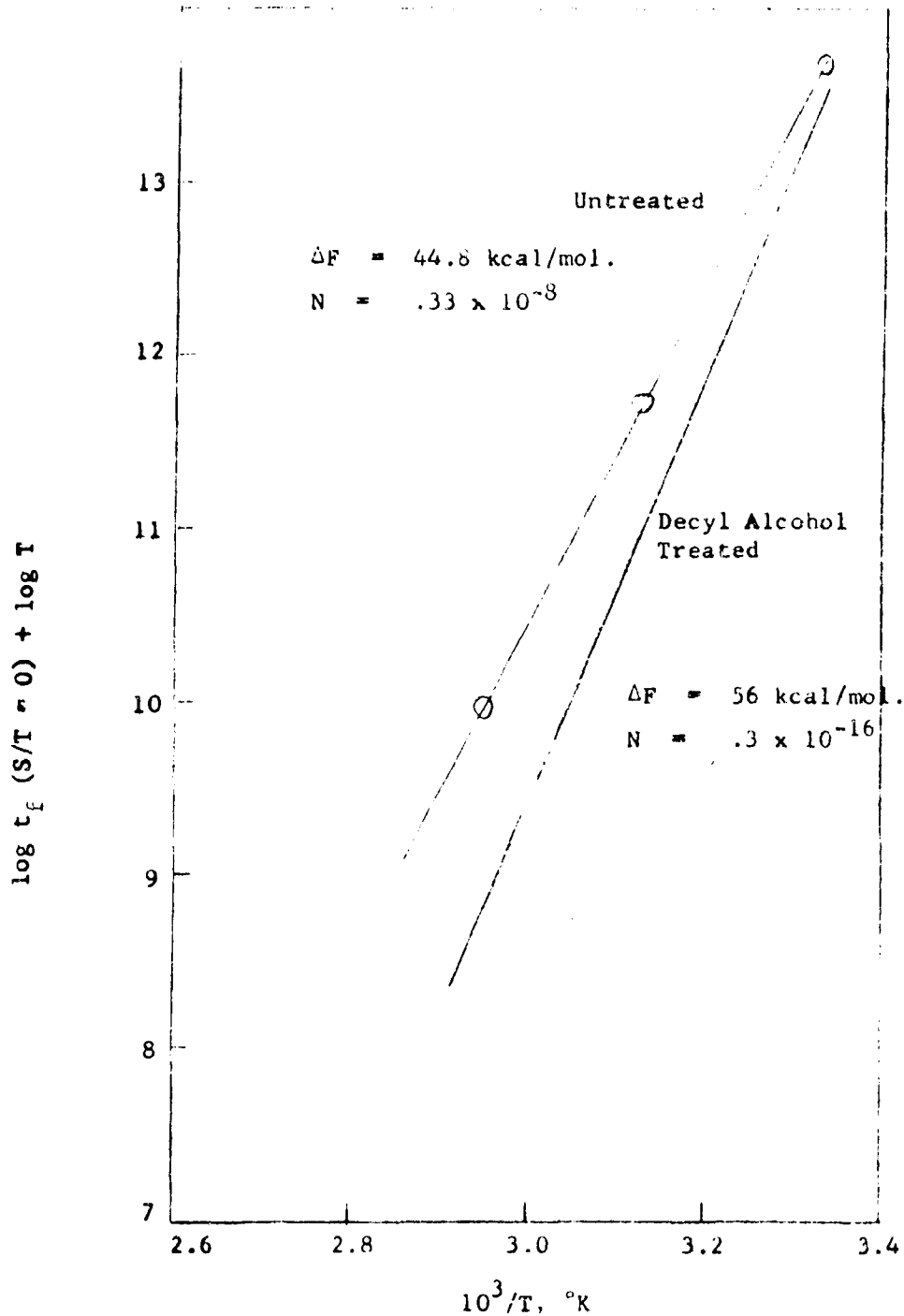
COMPARISON OF UNTREATED AND TREATED ISOTHERMAL
STRESS RUPTURE LIFE OF MARLEX 50 POLYETHYLENE

Untreated samples tested in air.
Tested samples have decyl alcohol applied to
stressed surface.
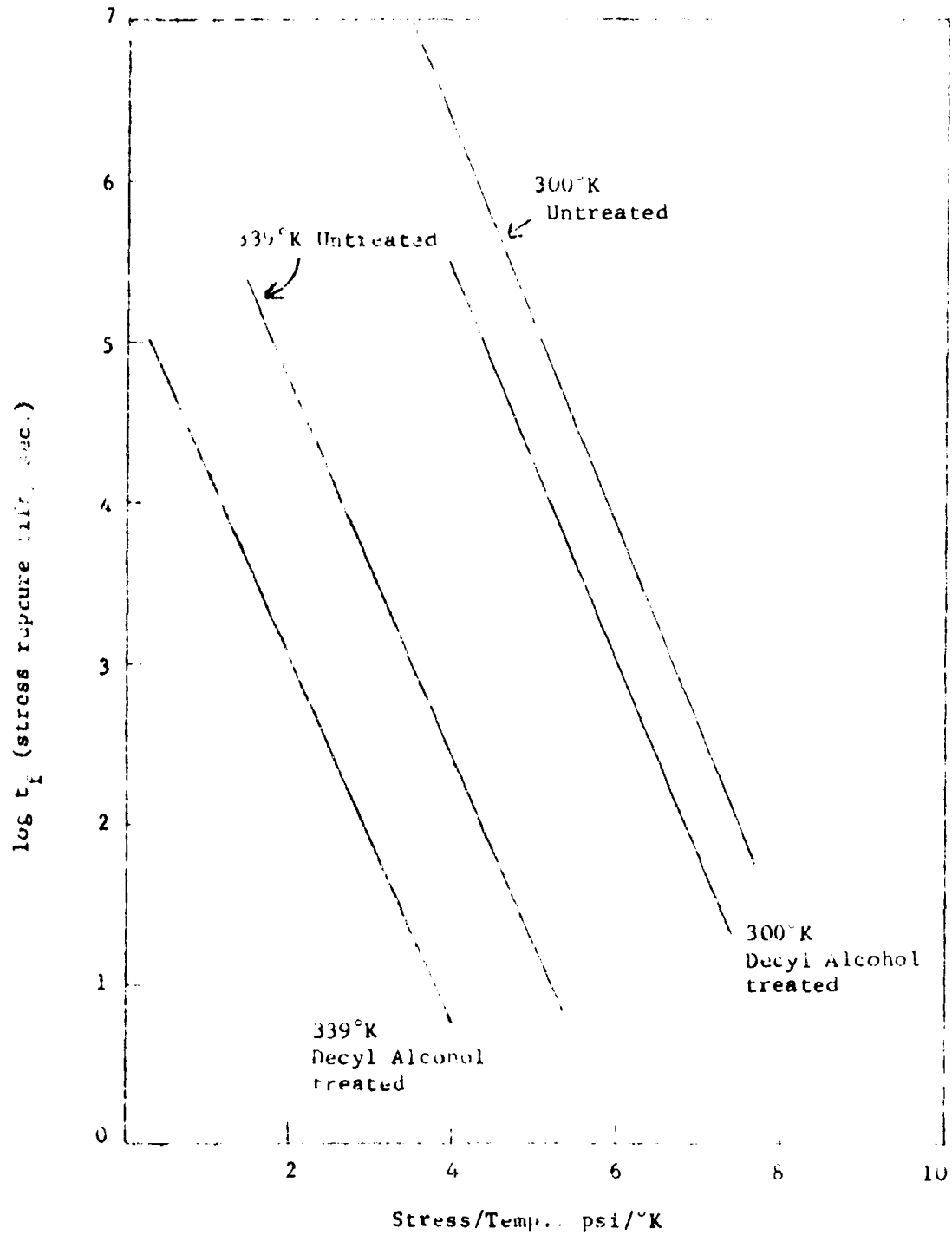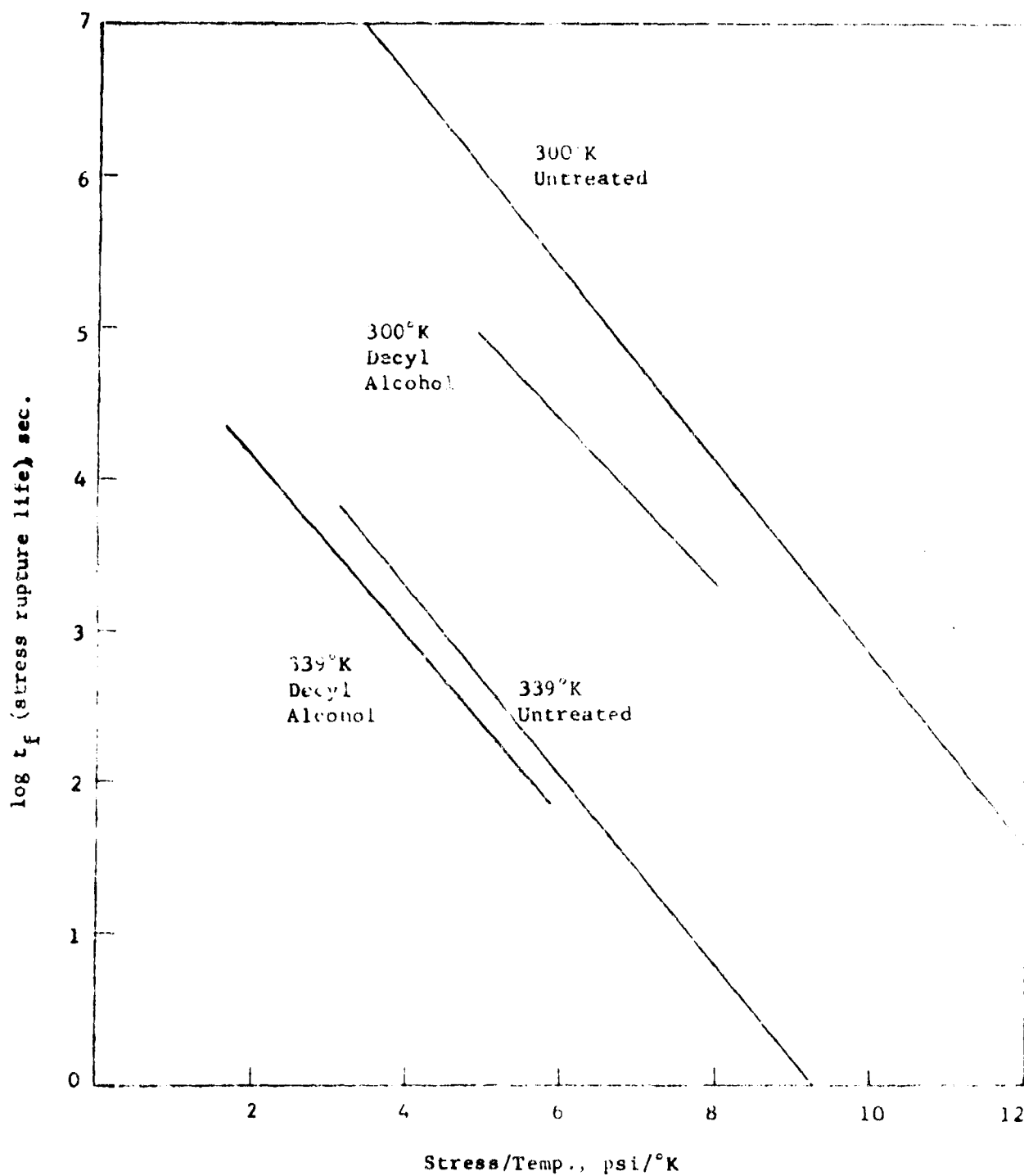
Figure A-3

ARRHENIUS PLOT OF POLYETHYLENE-MARLEX 6050 UNTREATED AND

TREATED WITH DECYL ALCOHOL
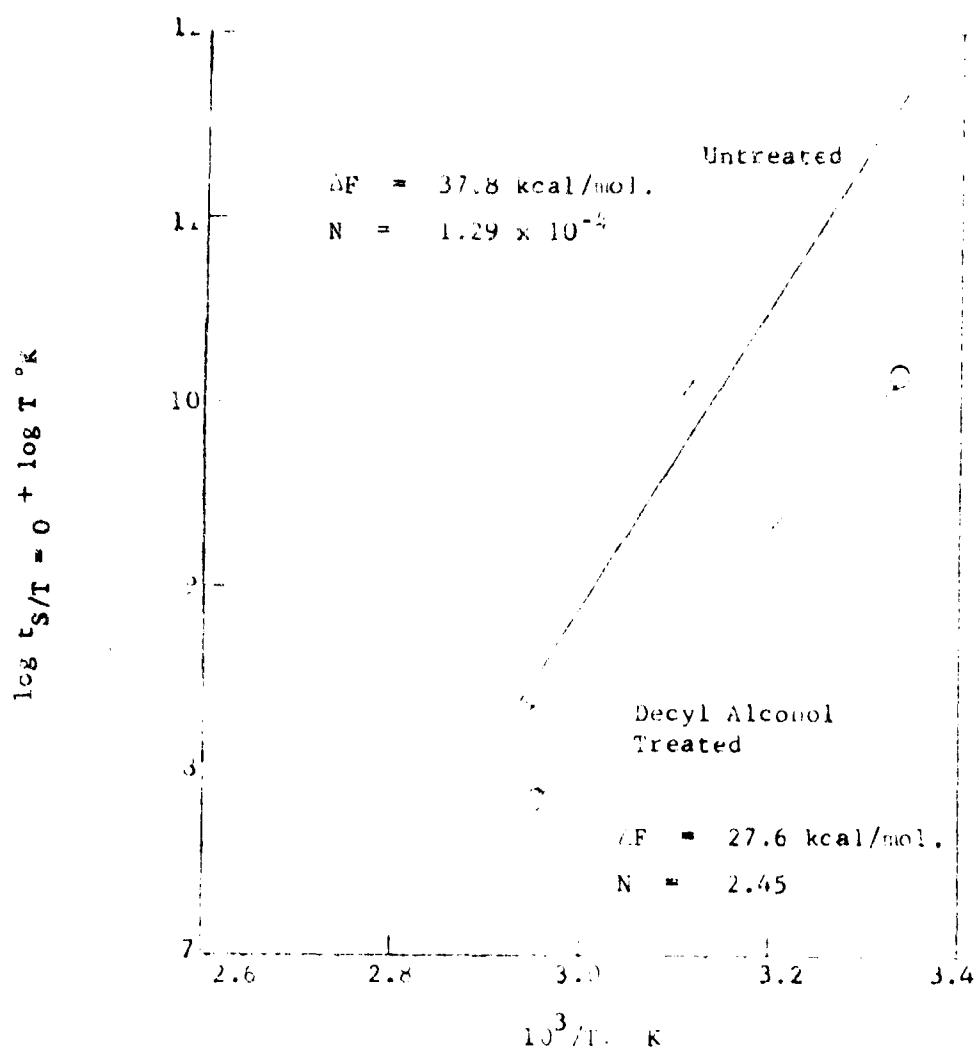
Figure A-4

APPENDIX B

Contents

Table B-1. Stress rupture tests with cracking agents having various substituents on benzene ring.

Table B-1

Stress Cracking - Substitution on (Benzene Ring) Structure

Material: SBR Tread Stock
Conditions: Cracking Agent on Surface
Temperature: $300°K$

Cracking Agent	Formula	Stress (psi)	Failure Time (sec.)
Nitrobenzene	$C_6H_5NO_2$	1080	20
		1080	24
		1080	15
		880	38
		880	28
		880	40
		680	73
		680	128
		680	344
		680	112
		480	1665
		480	1920
		280	16020
		280	10080
		280	17820
Chlorobenzene	C_6H_5Cl	706	25
		706	15
		706	6
		706	5
		706	3
		492	31
		492	186
		492	279
		492	33
		498	85
		498	54
		348	7144
		348	3847
		348	944
		287	4441
		287	5211
		287	6922
o-Dichlorobenzene	$C_6H_4Cl_2$	1080	15
		1080	22
		1080	22
		891	26
		891	6
		880	13

Cracking Agent	Formula	Stress (psi)	Failure Time (sec.)
o-Dichlorobenzene	$C_6H_4Cl_2$	688	93
		688	57
		688	345
		688	92
		492	1454
		492	898
		492	1063
		287	797
		287	6457
Tetrahydronaphthalene	$C_{10}H_{12}$	1230	7
		1230	5
		915	22
		915	25
		915	15
		603	522
		603	55
		603	840
		603	99
		603	260
		295	7220
		295	6444
		295	581
		292	891
		242	34170
		242	36230
		242	17282
		242	9000
		242	4050
		242	13150
Fluorobenzene	C_6H_5F	724	391
		724	24
		724	12
		724	503
		510	350
		510	687
		510	441
Bromobenzene	C_6H_5Br	698	50
		698	86
		698	79
		492	165
		492	1179
		492	903
		492	93
		492	543

Cracking Agent	Formula	Stress (psi)	Failure Time (sec.)
Bromoform	$CHBr_3$	705	29
		705	56
		705	16
		705	32
		500	758
		500	1782
		500	279
		500	111

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RESEARCH STUDY OF NEW CONCEPTS TO PROMOTE THE FAILURE OF POLYMERS BY STRESS CRACKING - Quarterly Progress Report Including Review of First Years Work

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

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13. ABSTRACT (U) This study is to develop a new concept on the failure of polymers by stress cracking. Results presented in this report cover the following work. Experiments have shown that failure time of treated samples is not influenced by sample size. Sets of material parameters for untreated and treated samples of SBR tread, Butyl tread and polyethylene have been obtained. Exploratory trials of cracking agents on Butyl tread produce a 10^7 reduction in failure time as was found for SBR tread. Cracking agents effective on tread stocks have little effect on polyethylene. An accelerated test for cracking effectiveness is being developed. Surface properties of polymers appear to have a specific influence in cracking effects. Computation of surface energy of polyethylene by three methods is in fair agreement and has established an important guideline in the mechanism of failure. Calculation methods for surface energies of binary mixtures was used to evaluate surface energy at maximum swelling of a vulcanized SBR stock. Experiments on spreading of organic liquids on SBR tread were used for an estimate of surface tension of the tread stock. Comparison of surface tension and solubility parameters of various polymers was made to show agreement with computed surface tension of SBR tread. Cracking tests with substituents on benzene ring are as effective as benzene.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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environment polyethylene						
cracking agents organic compounds						
applied stress aromatic						
reaction rate molecular structure						
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